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Telomers

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It has been shown (1) that the addition of halogenated methanes to olefins, in the presence of small amounts of peroxides or under the influence of ultraviolet light, yields products containing one or more equivalents of the olefin to one equivalent of halogenated methane.

$$RCH=CH_2 + CCl_4 \longrightarrow RCHClCH_2CCl_3$$
$$RCH=CH_2 + CBr_4 \longrightarrow RCHBrCH_2CBr_3$$
$$RCH=CH_2 + CHCl_3 \longrightarrow RCH_2CH_2CCl_3$$
$$RCH=CH_2 + CHBr_3 \longrightarrow RCH_2CH_2CBr_3$$

Carbon tetrabromide gives only one-to-one addition products, whereas products containing two or more equivalents of olefin to one of carbon tetrachloride often are formed in the addition reactions of carbon tetrachloride.

Chlorinated acids, or their derivatives, likewise form one-to-one addition products with olefins (2).

$$CH_3(CH_2)_5CH=CH_2 + Cl_2CHCOOCH_3 \longrightarrow CH_3(CH_2)_7CCl_2COOCH_3$$

$$CH_3(CH_2)_5CH=CH_2 + Cl_3CCOCl \longrightarrow CH_3(CH_2)_5CHClCH_2CCl_2COCl$$

Yield in the latter reaction is 81 per cent.

Ketones can be prepared directly by the addition of aldehydes to olefins. For example, the reaction of *n*-butyraldehyde to hexene-1 in the presence of acetyl peroxide yields propyl hexyl ketone.

Alpha, beta-unsaturated aldehydes can be prepared by hydrolysis of the addition products of bromodichloromethane to olefins.

$$CH_3(CH_2)_5CH=CH_2 + BrCHCl_2 \longrightarrow CH_3(CH_2)_5CHBrCH_2CHCl_2$$
$$\downarrow \text{hydrolysis}$$
$$CH_3(CH_2)_5CH=CHCHO$$

The reaction of one mole of dibromodichloromethane with two moles of olefin yields halides which can be hydrolyzed to substituted divinyl ketones (3).

$$2CH_3CH=CH_2 + CBr_2Cl_2 \longrightarrow CH_3CHBrCH_2CCl_2CH_2CHBrCH_3$$
$$\downarrow \text{hydrolysis}$$
$$CH_3CH=CHCOCH=CHCH_3$$

Organic compounds containing phosphorus (4) and silicon (5) are also obtainable through the peroxide-catalyzed addition of phosphorus trichloride or trichlorosilane to an olefin.

$$CH_3(CH_2)_5CH=CH_2 + PCl_3 \longrightarrow CH_3(CH_2)_5CHClCH_2PCl_2$$

$$CH_3(CH_2)_5CH=CH_2 + SiHCl_3 \longrightarrow CH_3(CH_2)_5CHClCH_2SiCl_2$$

Yield in the latter reaction is 99 per cent.

The value of this synthetic method is obvious. The products are valuable intermediates for further synthesis.

In particular, the type of reaction described above has been found useful in

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the development of a type of polymer called a *telomer*. The name is derived from the Greek *telos* meaning end and *meros* meaning part. Consequently, the process by which these compounds are produced is called telomerization. Thus, a compound, YZ, called a *telogen*, is treated under polymerizing conditions with more than one unit of a polymerizable compound having an ethylenic unsaturation. The resulting compounds have the formula, $Y-(A)_n-Z$, where (A) is a divalent radical formed by the polymerization of the ethylenic component, and n is greater than one; Y and Z are the components of the telogen. In the telomer, the components are not present in recurring units, as is the case in the usual polymer. The components, Y and Z, of the telogen appear only once in the molecule and always on the terminal carbons of the polymerized ethylenic component, whereas the olefinic component may occur many times. There is no recurring unit such as $YCH_2CH_2ZCH_2CH_2Y$.

Low Molecular Weights

As examples of the formation of relatively low molecular weight telomers the following may be listed:

a. The products resulting from the interaction of vinyl acetate and carbon tetrachloride have the general formula, $CCl_3[CH_2CH(OAc)]_nCl$, where n is an integer from 1 to 8. When $n=1$, the compound is a simple additive product, but when $n>1$, the products are telomers in which the end group is characteristic. Refluxing the components in the presence of benzoyl peroxide for 10 hours results in products of the above formula in which $n=1$ and 2 predominantly. Smaller amounts of higher telomers are also formed (6).

b. An invention similar to (*a*) involves the use of vinyl thiolacetate and ethylene. These components are reacted at 100°C. under a pressure of 900 atmospheres of ethylene to give a telomer having a molecular ratio of three moles of ethylene to one of vinyl thiolacetate. By treating the polymer with potassium hydroxide in methanol, hard, tough, insoluble films are formed, which remain infusible at temperatures as high as 250°C. (7).

c. Ethylene reacts with hydrochloric acid in the presence of a free radical to yield a mixture of alkyl chlorides. The distillable products comprise all of the straight-chain primary alkyl chlorides having an even number of carbon atoms from *n*-butyl chloride to eicosyl chloride. Higher alkyl chlorides are formed in increasing proportions as the ethylene pressure is increased (8).

Higher Molecular Weights

Following are examples of higher molecular weight telomers:

a. Products having the general formula, $H(CH_2CH_2)_nR$, where n is 22 to 54, are formed when ethylene is polymerized in the presence of various oxygenated compounds. The preparations are made in a stainless steel autoclave under a pressure of 800-1000 atmospheres of ethylene in the presence of benzoyl peroxide at 80°C. The following telomers are among those which have been described (9) (the figures after each compound giving the ratio of moles of ethylene to moles of compound): the telomers from ethylene and a) ethyl malonate, 39/1; b) ethyl acetoacetate, 35/1; c) methyl methoxyacetate, 47/1; d) 1,4-dioxane, 54/1; and e) 1,3-dioxolane, 22/1. These telomers are therefore considerably smaller in size than the usual polymer or copolymer. The products are soft to hard waxes, melting at 80-120°C., and are said to be useful as substitutes for carnauba wax.

b. Telomers of ethylene and acetals are compatible with paraffin and waxes over wide ranges of composition, possess high wax-solvent retention, form continuous hard films without stringing or sticking, and have good solubility characteristics. They are prepared by the

reaction of ethylene with an acetal under conditions like those given in (9). Thus, the telomer, ethylene-1,3-dioxolane, 46/1, is a soft wax which is excellent as a mold lubricant for vulcanization. A similar reaction with methylal gives a telomer containing 57 moles of ethylene and one mole of methylal. Small amounts of other olefinic compounds may be added to modify the telomer. An example of such a telomer that has been prepared is ethylene vinyl acetate 1,3-dioxolane, 115:3:5:1 (10).

c. Thio ethers of the telomeric type are formed by the interaction of sulfhydryl compounds (especially hydrogen sulfide) and ethylene. The reaction takes place at high pressures and temperatures (11).

$$n CH_2=CH_2 + H_2S \longrightarrow H(CH_2-CH_2)_{n-1}SC_2H_5$$

A similar invention involves the reaction of sodium dithionite with ethylene at 750 atmospheres pressure in the presence of benzoyl peroxide. A tough white polymer is obtained with a molecular weight of 17,000 (12).

d. Plaster- and rubber-like materials are obtained by reacting a diene with a haloalkane in the presence of benzoyl peroxide. Typical dienes for this are 1,3-butadiene, chloroprene, and 2,3-dimethyl butadiene. Typical haloalkanes are carbon tetrachloride, 1,1,1-trichloroethane, and chloroiodomethane (13).

e. Telomers containing aromatic nuclei may be converted to polysulfonic acids. For example, vinyl benzoate or styrene, when treated with a telogen such as carbon tetrachloride, forms telomers which, upon sulfonation, yield products having a 1:1 ratio of sulfuric acid groups to aromatic nuclei (14).

If these styrene-carbon tetrachloride telomers are treated with nitric acid, polynitro aromatic compounds are obtained. For example, the reaction of twenty parts of one of these telomers with 150 parts of fuming nitric acid gives a yellow product containing one nitro group per styrene unit. This compound may be reduced to the corresponding amine (15). The polysulfonic acids and the polyamino aromatic compounds thus formed are used as intermediates in the preparation of dispersing agents, surface-active agents, dyes, and pigments.

Mechanism

As has been stated, telomerization apparently proceeds *via* a free radical mechanism, as may be illustrated by the addition of methyl dichloroacetate to an aliphatic olefin.

$$RCH=CH_2 + CHCl_2COOCH_3 \xrightarrow{Bz_2O_2} RCH_2CH_2CCl_2COOCH_3 + RCH_2CH_2CHRCH_2CCl_2COOCH_3 + \text{telomers}$$

If diacetyl peroxide is the catalyst the reaction may be written as follows:

$$(CH_3COO)_2 \longrightarrow CH_3\cdot + CO_2 + CH_3COO\cdot \quad (A)$$

$$CHCl_2COOCH_3 + CH_3\cdot \longrightarrow CH_4 + \cdot CCl_2COOCH_3 \quad (B)$$

$$RCH=CH_2 + \cdot CCl_2COOCH_3 \longrightarrow R\dot{C}HCH_2CCl_2COOCH_3 \quad (C)$$

$$R\dot{C}HCH_2CCl_2COOCH_3 + CHCl_2COOCH_3 \longrightarrow RCH_2CH_2CCl_2COOCH_3 + \cdot CCl_2COOCH_3 \quad (D).$$

However, instead of step (D), the free radical formed in step (C) could react with an additional olefin molecule thus:

$$R\dot{C}HCH_2CCl_2COOCH_3 + RCH=CH_2 \longrightarrow R\dot{C}HCH_2CHRCH_2CCl_2COOCH_3 \quad (E).$$

The free radical product of reaction (E) may react again, either with methyl dichloroacetate as in equation (D) to form $RCH_2CH_2CHRCH_2CCl_2COOCH_3$, or n-1 times with additional olefin molecules as in (E) to form the higher telomer. $H(RCH\text{-}CH_2)_nCCl_2COOCH_3$ (16).

It is interesting to compare the decomposition of diacetyl peroxide in aliphatic acids (17). In this case only the methyl free radicals have sufficient energy to remove the α-hydrogen atoms of the acids. The dimerization of the new free radical occurs as a result of the fact that this radical is resonance-stabilized and requires a high energy of activation to react with the solvent.

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New Eastman Organic Chemicals

P 4077 N-Acetylethanolamine (Pract.) . . . . . 1 kg. . . $12.00 E
$CH_3CONHCH_2CH_2OH$ . . . MW 103.12

P 5922 N-Bromosuccinimide (Pract.) MP 175-177° dec. . . . . 100 g. . . 3.00 C
$COCH_2CH_2CONBr$ . . . MW 177.00

T 5454 Di-tert.-amylphenol (Techn.) . . . . . 2 kg. . . 3.20 G
$[(CH_3)_2C_2H_5C]_2C_6H_3OH$ . . . MW 234.37

P 3565 1,3-Diketohydrindene (Pract.) MP 131-133° . . . . . 10 g. . . 2.00 A
$C_6H_4COCH_2CO$ . . . MW 56.14

5524 2,6-Dinitro-4-chloroaniline MP 145-147° . . . . . 100 g. . . 4.00 C
$(NO_2)_2C_6H_2ClNH_2$ . . . MW 217.57

P 5950 Ethylenethiourea (Pract.) MP 198-200° . . . . . 500 g. . . 3.25 D
$CH_2CH_2NHCSNH$ . . . MW 102.16

5946 Ethyl Hydantoate MP 135-137° . . . . . 100 g. . . 9.00 C
$NH_2CONHCH_2COOC_2H_5$ . . . MW 146.15

526 Glutaronitrile BP 137-140°/10 mm . . . . . 100 g. . . 9.00 B
$CN(CH_2)_3CN$ . . . MW 94.11

2294 Hexamethylbenzene MP 164-166° . . . . . 10 g. . . 3.00 A
$(CH_3)_6C_6$ . . . MW 162.26

P 5932 Hexamethylenediamine (72%) (Pract.) . . . . . 1 kg. . . 4.55 E
$NH_2(CH_2)_6NH_2$ . . . MW 116.20

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$HO(CH_2)_5OH$ . . . MW 104.15